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Bio-oil valorization: A review

Kathlene Jacobson [a], Kalpana C. Maheria [b], Ajay Kumar Dalai [a,*]

[a] Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, Canada S7N 5A9
[b] Applied Chemistry Department, Sardar Vallabhbhai National Institute of Technology, Surat-395 007, Gujarat, India

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ABSTRACT

Fuels from biomass (biofuels) are used to mitigate the greenhouse gases produced through the utilization of fossil fuels. Non-edible or waste biomass can be pyrolyzed to produce bio-oil. The oil, an unstable and low energy product, can be further upgraded through hydrodeoxygenation to produce gas and/or diesel range hydrocarbons and value added chemicals. The objective of this review is to explore upgrading techniques that are currently being researched and utilized. This review reveals several aspects that in turn will serve as an aid for bio oil valorization, such as, evaluating characterization techniques involved in understanding salient features of bio-oil, insight of bio-oil pretreatment methods for water removal to increase heating values and decrease risk of catalyst poisoning in subsequent hydroprocessing, studies regarding model compound upgrading, reaction mechanism and finally, provides brief review of common catalysts for hydrotreatment of bio-oil in order to yield value added chemicals and fuels.

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* Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777.
E-mail address: ajay.dalai@usask.ca (A. Kumar Dalai).

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1. Introduction

Hydrocarbons, especially liquid and gaseous fuels, are vital to the transportation industry. Traditionally, the desirable hydrocarbons are produced from fossil fuel sources. However, the continuous use of fossil fuels for hydrocarbon and energy sources has caused severe global problems through increasing the concentration of carbon dioxide (CO_2) in the atmosphere.

Of primary concern, is the current availability of such sources; fossil fuels are being consumed without replacement, creating a volatile market with ever increasing prices. The consumption of fossil fuels caused gradual depletion of world's accessible oil reservoirs. Companies are failing to find new reserves of oil sufficient to meet the future need. Most oil producers are investing in more capital-intensive projects, needing to drill in remote places and deeper to obtain oil. The extensive use of fossil fuels and related chemicals introduces greenhouse gases, such as, CO_2, chlorofluorocarbons (CFCs) and methane into the atmosphere causing the "greenhouse gas effect". This second problem of global warming effect of CO_2 and other greenhouse gases on the environment has generated a lot of public and political concern. Renewable energy resources can be one of the potential alternative solutions to fossil fuels and their derivatives. They have become a large focus of research, as energy sources due to their reduced environmental risks and pollution. In addition to their sustainable favorability, renewable energy resources are, in general, more evenly distributed over earth's surface than fossil fuels and may be exploited using less capital-intensive technologies. Hence, they increase the scope for diversification and decentralization of energy supplies and the achievement of energy self-sufficiency at a local, regional, and national level [1].

Biomass is one such promising alternative and has a worldwide abundance. Despite the complexity associated with biomass as a feed for bio-oils, the use of biomass is rapidly expanding. Several industries have commercialized the production of so-called first generation bio-fuels, bio-ethanol from sugar-like products (sugar, starch, etc.) and bio-diesel (from rapeseed, sunflowers, etc.). However, the scale of production of these first generation biofuels in bio refineries appears to be several times lower than typical unit operations in refineries (few barrels a day compared to thousands of barrels per day in conventional refineries) [2]. Besides, these feeds are in competition with the food industry, which may raise ethical questions as well.

Thus, there is a demand for a second generation of biofuels. Lignocellulosic feed stocks (wheat straw, rice straw, corn, sugarcane bagasse etc.), non-food crops and wood are energy crops, which are converted into second generation bio-refineries. Possible biofuel conversion technologies of said biomass are: fermentation processes (conversion of the cellulosic materials to low molecular weight sugars through chemical and/or physical processes; then, subsequent conversion to ethanol via fermentation), gasification to produce bio-syngas for further upgrading to methanol or gas/diesel, or liquefaction with further upgrading either through gasification or deoxygenation, hydrogenation etc. to produce gas and/or diesel range hydrocarbons and value added chemicals. Bio-oil obtained through fast biomass pyrolysis technique is also considered as one of such second generation bio-fuel. Though, it exhibits higher energy content than biomass and is considered to be easy transportable source of fuels and chemicals, it needs to be upgraded for further use as engine fuel, owing to its high instability, viscosity, polarity and corrosiveness [3]. Low heating values than petrofuels and immiscibility with petrofuels prevents use of crude bio-oil as a fuel additive for some boilers and engines [3–5].

Nevertheless, biomass is still not widely used for biofuel production. The main reasons are the presence of contaminants (including ash, water, and oxygen), the variation in chemical composition, and its low energy density. To overcome these issues, an indirect approach seems advantageous. A possible indirect approach would be the conversion of biomass into a more uniform and stable structure, after which secondary conversion processes, would transform the intermediates into transportation fuels and value added chemicals. The primary conversion process referred to, in this introduction, is the pyrolysis (fast) of biomass. Here, the biomass is subjected to rapid heating to temperatures in the range of 450–650 °C with a residence time of <2 s in an oxygen free atmosphere [6]. Incomplete degradations occur, which yield three major products: char (mostly carbon which can be employed to enrich soil, as a source for activated carbon, or as a solid fuel additive), fuel gas (usable in any combustor or syngas feed), and liquid oil to be further upgraded to a bio-fuel.

In recent years, the liquid products obtained from pyrolysis of biomass have received considerable attention. However, the important aspect is that, these liquids from biomass are not useful as fuels except as direct boiler applications and possibly for some types of turbine and large diesel applications after being modified [7]. In order to make bio-oil to be useful as transportation fuel, it requires chemical transformation to increase thermal stability and reduce volatility, viscosity through oxygen removal and molecular weight reduction. Further, bio-oil does not naturally blend with conventional petroleum fuel. It may be possible to add a solvent or to emulsify mixtures of bio-oil and fuel oil in order to get homogeneous blends. Apart from catalytic cracking and hydrotreating, organic solvents addition and emulsification are also reported as one of the way to improve the quality of the bio-oil [8,9]. However, organic solvent utilization is associated with handling and disposal problems and emulsification of bio-oil with diesel provides a short-term approach to the use of bio-oil in diesel engines. Moreover, fuel properties such as heating value, cetane value and corrosivity are not satisfied. This leaves two feasible avenues for bio-oil upgrading: atmospheric pressure upgrading (catalytic cracking) and high pressure upgrading (hydrotreating) [10,11].

Catalytic cracking is a conventional petroleum reforming process, capable of decomposing heavy fractions into medium and light distillates. The process occurs in the presence of an acidic and preferably hydrophobic catalyst, typically ZSM-5, to produce H_2O, CO_2 or CO under atmospheric pressure. The same technology can be applied to the reforming of highly oxygenated and bulky bio-oil. The high temperatures associated with this process, are able to cleave bonds in the larger molecules as well as deoxygenate compounds present in the pyrolysis oil, and produce desirable (generally aromatic) fuel-range hydrocarbons. Atutxa et al. [12] have successfully applied HZSM-5 in the deoxygenation of the bio-oil in their investigation on catalytic pyrolysis of biomass (Pinus insignis) over H-ZSM-5 zeolite, in a spouted bed reactor.

Hydrotreating (HDT) is another conventional form of petroleum hydroprocessing technology. It is generally used to saturate olefins and aromatics and remove contaminants (sulfur, nitrogen, metals),

to produce a clean product for further processing or finished product. Commonly in industry, HDT utilizes bi-metallic acid catalysts such as $CoMo/\gamma-Al_2O_3$ and $NiMo/\gamma-Al_2O_3$ to remove sulfur and/or nitrogen from heavy gas oil through hydrodesulphurization (HDS) and hydrodenitrification (HDN) [13–15], respectively. In the case of bio-oils, neither sulfur nor nitrogen is present in significant quantities, but oxygen is abundant. Therefore, hydrotreatment of bio-oils is needed for the removal of oxygen through hydrodeoxygenation (HDO). HDO and HDN are very similar due to the overlapping nature of nitrogen and oxygen molecules. Thus, HDT of bio-oil incorporates the same principles and process technology as HDT of conventional petroleum feeds. Hydrocracking is a similar process with higher temperatures utilizing noble metal catalysts such as $Pt/\gamma-Al_2O_3$ or $Pd/\gamma-Al_2O_3$.

The most common obstacle while using either HDO or catalytic cracking as the upgrading method is that, the yield of upgraded bio-oil is relatively low and the problem of catalyst deactivation and reactor clogging arises due to production of large amount of char, coke and tar [10]. The coking can be so severe that it plugs fixed-bed reactor systems resulting in termination of experimentation [16]. Desirable product yield can be increased while decreasing the undesirable carbon deposition by co-feeding hydrogen donors as well as modifying the reactor systems. The most common co-feeds are methanol, tetralin, and decalin. The hydrogen donors not only promotes cracking and hydrogenation reactions but also, serves to dilute the lignin and decrease polymerization at high reaction temperatures, in turn, contribute in reducing volatile nature of the bio-oil.

Recently, Tang and coworkers have introduced a novel way to upgrade bio-oil with the combination of hydrotreating, esterification and cracking under supercritical conditions. The crude bio-oil was upgraded in supercritical ethanol under hydrogen atmosphere, using hydrotreating catalyst (palladium) supported on acidic sites (SO_4^{2-}/ZrO_2/SBA-15). In this case ethanol acted as both, reactant and reaction medium. They have found not only improved quality of bio-oil (obtain increased pH and heating values, decreased kinematical viscosity and density values) but also reduced aldehyde and ketones present in bio-oil too as they are converted into stable compounds with the aid of hydrotreating catalyst. It is to be noted here that, aldehydes and compounds with unsaturated carbon bond in bio-oil are active for polymerization and condensation reactions. These reactions increase viscosity and are responsible for phase separation in bio-oil, as well. Prevention of such reactions inhibited the formation of tar or coke. Esterification reaction is used as an effective way to convert unwanted acid present in bio-oil into the esters [17].

The field of catalytic processing of bio-oil from pyrolysis to liquid provides the largest basis for this review. As such, the review does not provide details of the pyrolysis process. The reader may refer to the pyrolysis review by Mohan et al. [18]. This review highlights developments from 1980 to 2006, based on available data from the literature, in the field under study. In the first section, pyrolysis oil properties from various feedstocks will be discussed in an attempt to further understand the necessity of bio-oil upgrading. In the second section, the effects and benefits of various reaction equipment is outlined. Subsequently, model compound studies to date will be summarized. Then, both atmospheric and high-pressure upgrading experimentation using crude pyrolysis oils to obtain liquid fuels in gasoline or diesel range via catalysis is discussed. Finally, the advantages of co-feeding hydrogen donor solvents are discussed.

2. Pyrolysis oil composition and properties

2.1. Fast pyrolysis for bio-oil production

Pyrolysis is thermochemical decomposition of biomass into bio-oil, solid charcoal and gaseous products in the absence of air/oxygen at temperature range of 350–525 °C and pressure 1–5 atm [19]. Fast pyrolysis, is the most common method of converting biomass into bio-oil, in which, residence time is shorter than one second and temperature is around 500 °C, favoring the formation of liquid pyrolysis oil [20,21]. Pilot or large-scale biomass pyrolysis operations such as Dynamotive, Advanced Biorefinery Inc, and Ensyn utilize Waterloo Fast Pyrolysis Process technology (WFPPT). Biomass pyrolysis technologies have already been commercialized [22,23]. The largest commercial plant, producing bio-oil (200 t biomass/day) was constructed by DynaMotive in 2007 [24,25].

In this system, the biomass is fed into the fluidized bed using a variable twin speed screw feeder. It allows recycled product gas to be used as the fluidizing gas. It operates at temperatures of 450 °C+, atmospheric pressure, and low residence times of 0.3–1.5 s and N_2 is used as a carrier gas. The prime end products of pyrolysis are; a hydrogen-enriched gas, a hydrogen-deficient oil (thick dark-brown liquid also known as bio-oil), and a carbon-rich solid known as char. Optimum yields (total liquids) from WFPPT have been reported at 75 wt% of dry feed at a heating rate of 105 °C/s and short residence times [26]. The present discussion will focus solely on the oil obtained.

2.2. Bio-oil properties

Bio-oil produced from fast pyrolysis possesses high viscosity, thermal instability and corrosiveness. These undesirable properties generate obstacles to the substitution of fossil fuels by bio-oils. Furthermore, any variations in the pyrolysis process can yield very different bio-oils. Several studies reported that, the parameters such as, feedstock chemical composition, particle size, moisture content, pyrolysis temperature, and heating rate, significantly, affect the bio-oil yield and properties [27–32]. Further, according to Huber et al. [22] the exact composition of the bio-oil is dependent upon the type and quality of the feedstock (including dirt and moisture content), organic nitrogen or protein of the feedstock, heat transfer rate and final char temperature during pyrolysis, time and temperature of vapors in the reaction, efficiency of the char removal system and the condensation equipment (to recover the volatile components from the non-condensable gas stream). Therefore, characterization of bio-oil is beneficial in understanding the kind of bio-oil upgrading needed to produce quality transportation fuels and chemicals.

Because of the original complexity of biomass and variation in cellulose, hemicellulose and lignin content, the composition of the bio-oil is slightly unpredictable and contains a plethora of constituents. Huber et al. [22] reported bio-oil to contain acids (including acetic and propanoic), alcohols (methanol, ethylene glycol, ethanol), ketones (acetone), aldehydes (acetaldehyde, formaldehyde, ethanedial), miscellaneous oxygenates (glycolaldehyde, acetol), sugars (1,6-anhydroglucose, acetol), furans (furfurol, furfural), phenols (phenol, methyl phenol, dimethyl phenol), and guaiacols (isoeugenol, eugenol, 4-methyl propyl syringol) irrespective of source of biomass.

The multicomponent bio-oil mixtures are derived primarily from depolymerization and fragmentation reactions of the three building blocks of lignocellulosic biomass: cellulose, hemicellulose, and lignin. The phenols, guaiacols, and syringols are formed from the lignin fraction, whereas the miscellaneous oxygenates, sugars, and furans are produced from the cellulose and hemicellulose. The esters, acids, alcohols, ketones, and aldehydes probably form from the decomposition of the miscellaneous oxygenates, sugars, and furans [22].

2.3. Bio-oil characterization techniques

Current literature on bio-oil characterization focuses on determination of chemical composition and fuel characteristics [27,33–37].

Different fuel characteristics such as kinematic viscosity, flash point, density, water content, and pH were documented [34–36]. Several attempts have been well documented in the literature to characterize bio-oil, derive its composition, and compare its fuel characteristics with conventional petroleum derived fuel. The most notable differences between the two types of fuels are the higher oxygen and water content associated with bio-oil, as well as the acidic pH. Bio-oil production with lower water content is favored for prolong stability of bio-oil in storage. Bio-oil contains 15–30 wt% water, although up to 60% is reported [38], which is derived from the original moisture in the feedstock and forms as a product through dehydration during the pyrolysis reaction as well as during storage [27,33–37]. The presence of water lowers the heating value and viscosity, enhances fluidity, which is desire for the atomization and combustion of bio-oil in the engine. The amount of water present in bio-oil is mostly depends on type of biomass. In some cases, biomass contains high percentage of water with a low calorific value and is not considered as a suitable candidate for fuel application [38]. Hence water content determination of bio-oil is essential before its consumption as biofuel. Water content is usually determined by Karl Fischer method, most recently, Ragauskas et al. have used ^{31}PNMR technique [39].

Bio-oil is a complex mixture of oxygenated compounds. The oxygen content in bio-oil is typically 35–40% [34,36] and is distributed in more than 300 compounds depending on the source of biomass and adapted pyrolysis conditions such as mode of pyrolysis, type of pyrolysis system, temperature, residence time etc. The presence of oxygen creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content of bio-oil enhances combustion characteristics which eventually help to reduce the amount of carbon dioxide emissions/pollution produced when bio-oil is burned as a fuel. On the other hand, the low oxygen content leads to higher energy density and two fold increase in miscibility with hydrocarbon fuels as compared to conventional fuel [33]. Instability in bio-oil arises from presence of strong acidity, resulted from the high concentration of organic acids present in bio-oil. Such a high concentration of organic acids makes complex composition of biomass in turn widens the boiling temperature range. Polymerization of some reactive components occurs upon slow heating and bio-oil start boiling below 100 °C and ends at 250–280 °C leaving around 35–50% of solid residues. Thus, owing to presence of high concentration of organic acids, the bio-oil gets completely evaporated before combustion. This is undesirable and creates an obstacle for bio-oil to be a good fuel. The typical properties of bio-oil obtained by fast pyrolysis of wood are compared with heavy fuel oil in Table 1.

The chemical composition is commonly identified through chromatographic techniques such as GC, GC–MS, and other spectroscopic techniques including 1HNMR, FT-IR, and CHNS [27,35]. An example of flax straw derived bio-oil chemical compound identification using coupled GC and GC–MS spectroscopic techniques is shown in Table 2. In this case, only the most plentiful compounds were identified using GC–MS and quantified using GC. Table 3 depicts a model chemical group classification of bio-oil carried out through GC, GC–MS, FT-IR, and 1HNMR, for bio-oil derived from a biomass mixture of wheat–wood sawdust [38]bio-oil. A summary of both the physical and chemical bio-oil characterization techniques is depicted in Table 4.

Table 1
Typical properties of wood pyrolysis bio-oil and of heavy fuel oil [34].

Physical property	Bio-oil	Heavy fuel oil
Moisture content (wt%)	15–30	0.1
pH	2.5	–
Specific gravity	1.2	0.94
Elemental composition (wt%)		
C	54–58	85
H	5.5–7.0	11
O	35–40	1
N	0–0.2	0.3
Ash	0–0.2	0.1
Heating value (MJ/kg)	16–19	40
Viscosity (at 50 °C) (cP)	40–100	180
Solids (wt%)	0.2–1	1

Table 2
GC–MS liquid pyrolysis products from flax straw [40].

Compound	Retention time (min)	Area (%)
1-Hydroxy-2-butanone	6.47	1.93
2,3-Butanedione	1.86	1.34
2,3-Pentanedione	2.52	0.51
2-Cyclopenten-1-one	6.11	0.57
2-Cyclopenten-1-one, 2-hydroxy-3-methyl	11.70	1.25
2-Cyclopenten-1-one, 2-methyl	6.23	0.57
2-Cyclopenten-1-one, 3-methyl	8.17	0.74
2-Furfanol, tetrahydro-2-methyl	18.71	3.29
2-Methoxy-4-vinylphenol	19.34	0.73
2-Propanone, 1-(acetyloxy)	7.53	0.85
2-Propanone, 1-hydroxy	5.60	4.07
2-Furanmethanol	9.87	1.87
3-Pyridinol	32.76	0.86
Acetaldehyde	0.97	1.00
Acetic acid	6.95	20.87
Acetic acid, methyl ester	1.18	1.63
Acetone	1.15	1.06
Butyrolacetone	9.48	1.07
Cyclopropyl carbinol	16.08	1.62
Formic acid, ethyl ester	1.44	5.41
Furan, tetrahydro-2-(methoxymethyl)	8.02	2.01
Furfural	7.47	1.42
Phenol	14.35	ND
Phenol, 2.6-dimethoxy	22.30	1.25
Phenol, 2-methoxy	12.05	2.71
Phenol, 2-methoxy-4-methyl	13.38	1.17
Phenol, 4-ethyl-2-methoxy	14.70	0.73
Propanoic acid	8.28	1.97

[a] ND: not detected.

Table 3
Chemical classification of bio-oil produced from the fast pyrolysis of biomass mixture wheat-hemlock mixture [38].

Chemical classes	Amount present in bio-oil (%)
Hydrocarbons	2.6
Low molecular wt fatty acids/esters	13.7
Hexodecanoic acid	23.6
Furanoids	3.2
Pyranoids	1.2
Benzenoid hydrocarbons	2.6
Oxygenated benzenoids	14.6
Low mol. wt alcohols/aldehydes/ketones	1.7
High mol. wt alcohols	19.5
High mol. wt waxy components	2.1

Table 4
Summary of bio-oil characterization methods.

Characterization technique	Purpose of technique
Bomb calorimetry	To calculate the calorific or heating value
FT-IR	To identify functional groups
C, H, N, S, O analysis	To quantify the elemental composition and derive an approximate empirical formula
1H NMR	To determine chemical bonding within molecules
GC–MS	To identify and quantify chemical compounds present

It is to be noted here that, the high percentage of water (15–60%) found in bio-oil is the most detrimental characteristic in the development of transportation fuel from bio-oil [25]. Water's low reactivity, close azeotrope with many bio-oil constituents, and catalyst poisoning capabilities provide many obstacles. Thus, as discussed earlier in the text, in order to get the most energy and value from bio-oil, water must be removed before upgrading into desirable transportation fuels. The different methodologies implemented to remove the water from bio-oil are described in Section 3, in detail.

3. Bio-oil pretreatment methods

Water removal, as a means of pretreatment, will improve the bio-oil's properties (e.g. viscosity, heating value, density) and reduce the risk of catalyst poisoning in bio-oil upgrading, especially in the case of a noble metal catalyst. In literature, water removal from bio-oil has been attempted in four methods: distillation, dehydration, reactive rectification, and physiochemical separation.

3.1. Distillation and dehydration

The bio-oil is heat sensitive and subject to re-polymerization, so it cannot be fractionated by distillation [41]. Water removal from bio-oil via dehydrated Na_2SO_4 was attempted with a ratio of Na_2SO_4 to bio-oil of 3:1. This method only partially removed the water from bio-oil and the ultimate analysis of Na_2SO_4 treated bio-oil showed high sulfur (1.6%) content [38].

3.2. Reactive rectification

Junming et al. [10] reported that esters (e.g. ethyl formate, b.p. 327.8 K) had a lower boiling point than its corresponding acids (e.g. formic acid, b.p. 373.7 K); hence it was possible to convert low-molecular-weight acids with alcohol into esters and separate them from original bio-oil by reactive rectification. Surprisingly, with the separation of volatile organic acids, it was found that the H_2O and nonvolatile compounds form a phase separation (creating fractions of 'light oil' and 'heavy oil') [10]. Reactive rectification capitalizes on water and organic acids having higher polarity than the other major constituents in bio-oil. Their results showed that this method was able to reduce the water content in the bio-oil from 33 wt% to 11 wt%.

3.3. Additional water for fractionation

Bio-oil from pyrolysis is composed of phenolic lignin decomposition products together with water and a plethora of compounds of many classes. This makes fractional distillation of bio-oil impossible. Therefore, bio-oil solvent fractionation seems to be a very important topic to consider. The most common solvent utilized in literature is water. When an excess of water is added to bio-oil, two layers form. The top layer is the aqueous fraction where the highly polar compounds of bio-oil (acid, esters, etc.) settle as well as many carbohydrate-derived compounds. Through the addition of excess water, an organic fraction with approximately 2% water may be obtained. The bottom layer is a viscous, oligomeric, lignin-containing fraction. Upgrading work on the aqueous fraction has been well documented [18,38,42]. Because it is rich with carbohydrates, it serves as an excellent feed for the fermentation of alcohols. The commercialization of the lignin-rich fraction has not yet been explored. However, utilization of lignin in place of phenol for the preparation of phenol formaldehyde resins has been investigated.

Table 5
Proximate analysis, ultimate analysis, calorific value and pH of wheat-hemlock biomass, bio-oil and supercritical CO_2 fractions of bio-oil [38].

Samples	Proximate analysis (%)				Ultimate analysis (%)					H/C molar ratio	O/C molar ratio	Empirical formulae[3]	Calorific value (MJ/kg)	pH
	Moisture	Ash	Volatile matter	Fixed carbon1	C	H	N	S	O_2					
Wheat-hemlock biomass	8.3 ± 0.2	1.8 ± 0.1	83.0 ± 0.2	6.9 ± 0.2	46.7 ± 0.2	6.4 ± 0.2	0.05 ± 0.02	0.01	46.8 ± 0.3	1.64	0.75	$CH_{1.64}O_{0.75}N_{0.0009}$	18.6 ± 0.2	–
Crude bio-oil	59.1 ± 0.9	0.03 ± 0.1	–	–	19.3 ± 0.1	9.2 ± 0.1	0.74 ± 0.02	0.17	70.6 ± 0.2	5.72	2.74	$CH_{5.72}O_{2.74}N_{0.033}$	ND	2.8 ± 0.2
10 MPa fraction	0.5 ± 0.1	–	–	–	75.8 ± 0.2	11.9 ± 0.1	0.01	ND	12.3 ± 0.2	1.88	0.12	$CH_{1.88}O_{0.12}N_{0.0001}$	45.0 ± 0.4	4.5 ± 0.1
25 MPa fraction	1.5 ± 0.2	–	–	–	74.6 ± 0.3	11.5 ± 0.2	0.02 ± 0.01	0.01	13.8 ± 0.3	1.85	0.14	$CH_{1.85}O_{0.14}N_{0.0002}$	43.2 ± 0.2	4.3 ± 0.1
30 MPa fraction	3.1 ± 0.3	–	–	–	76.0 ± 0.2	11.7 ± 0.1	0.09 ± 0.01	0.02	11.9 ± 0.4	1.85	0.12	$CH_{1.85}O_{0.12}N_{0.001}$	38.8 ± 0.5	4.0 ± 0.1

ND: Not detected, 1% of fixed carbon calculated from difference of moisture, ash and volatile matter content, 2% of O calculated from the difference of C, H, N and S, 3S not taken into consideration.

Table 6
Yield and chemical classes of pyrolysis oil and its fractions [38].

Bio-oil and bio-oil fractions	Yield (%)	Chemical classes									
		Low mol. wt fatty acids/ esters	Fura- noids	Pyra- noids	Benzenoid hydro- carbons	Oxygenated benzenoids	Low mol. wt alcohols/ ketones	Hydro– carbons	Hexade- canoic acid	High mol. wt alcohols	High mol. wt waxy components
Bio-oil	–	2.6	13.7	23.6	3.2	1.2	2.6	14.6	1.7	19.5	2.1
Benzene	10.9	4.0	10.6	0–4	11.8	39.3	0.7	17.4	5.6	0.3	2.8
Et_2O	13.5	6.3	6.2	1.4	12.8	30.6	0.2	18.2	6.4	0.4	2.5
$CHCl_3$	24.0	7.4	7.0	2.3	14.0	19.9	0.4	22.8	5.8	0.8	3.7

3.4. Supercritical CO_2 extraction

The separation of water from bio-oil is essential to increase fuel efficiency as water content present in bio-oil affects many of the physicochemical properties as already discussed earlier. The separation technique is more advantageous than conventional extraction methods using organic solvents. Among different processes, the SC–CO_2 extraction is quite advantageous. The SC–CO_2 is most efficient alternative for upgrading bio-oil without catalyst [38]. In SC–CO_2 extraction, organic solvent is fairly replaced with SC–CO_2, a green solvent, while avoiding handling and waste disposal problem associated with organic solvents and thus, can be qualified as a green technology for extraction of valuable compounds from crude bio-oil. The SC–CO_2 extracted bio-oil can be used in renewable fuel to meet energy demands [38]. Rout et al. [38] attempted separation of valuable components from bio-oil by SC–CO_2 for the first time. The SC–CO_2 extract gave improved yield, selective extraction of product with temperature and pressure, a less acidic and moisture free product. Further, fractionated bio-oil has high calorific values as compared to diesel oil. A wheat-hemlock biomass mixture was converted to bio-oil through pyrolysis at the Advanced Biorefinery Inc. in Ottawa, Canada. The yields of the SC–CO_2 extracts were 4.3%, 13.2% and 15.2% corresponding to 10, 25 MPa and 30 MPa, respectively. The remaining bio-oil was waxy residue. Characterization methods for the biomass, crude bio-oil, and the three fractions are summarized in Table 5. It was observed that the calorific value of the bio-oil SC–CO_2 fractions was higher than the calorific value of the original biomass. Similarly, the ultimate analysis of CO_2 fractions indicated that the carbon percentage was increased with decreased percentage of oxygen as presented in empirical formulae. Therefore, the SC–CO_2 extraction process was successful as a pretreatment method. The extracts contained a low percentage of moisture along with high percentage of carbon.

Rout et al. [38] also explored the conventional process of extraction of organic compounds by column chromatography. Extractions of benzene, ethanol and chloroform were carried out. From Table 6, we can examine the yields as well as chemical shift from crude-bio-oil to the extracted fraction. It can be concluded that, the chloroform extraction was the most successful in obtaining pretreated oil because of its higher yield and chemical composition. The higher concentration of hydrocarbons makes it highly desirable.

4. Catalysts

Hydroprocessing catalysts are quite versatile, exhibiting activity for a number of important reactions. Those of major interest in hydroprocessing are removal of heteroatoms, via hydrodesulphurization (HDS), hydrodenitrification (HDN), hydrodemetallation (HDM), and for coal or biomass-derived liquids, hydrodeoxygenation (HDO) [15,43,44].

4.1. Advantages of zeolites

γ-Alumina is the most commonly used support for hydroprocessing catalysts in petroleum industry. γ-Alumina's desirable properties include strong mechanical and textural properties, great dispersion of active transition metals, and low cost [45]. However, negative aspect of γ-Alumina is the strong chemical interaction between the alumina and the transition metal catalysts in their oxide phase. This can make the transition of the catalyst metal to its active phase a difficult procedure and can prevent the catalyst from reaching its maximum potential activity [46]. The quest for superior support system that avoids the main disadvantages of alumina has led researchers to explore alternative support materials. In the past couple of decades, use of different porous materials such as carbon and zeolites of different topologies and mesoporous materials have received considerable attention [47,48] for use as a catalyst support. There has especially been a growing interest to use porous materials as a support for hydrotreating processes due to many unique attributes linked with such materials: high surface area, large variety of pore sizes, variable surface functional groups, easy metal recovery by the burning of the support, reduced coking propensity and resistance to nitrogen poisoning. Zeolites are among the most popular of these porous materials.

4.1.1. Zeolite shape selectivity and acidity

Zeolites are crystalline microporous silica based materials which are extensively used as heterogeneous catalysts in industry. They offer a well-defined and ordered pore structure on a molecular level. By choosing the appropriate organic template and synthesis conditions, the pore size and pore shape (dimensionality, intersections, and cages) may be directly influenced. The acidity of the zeolite may also be controlled through various methods such as silicon/aluminium (Si/Al) ratio, ion exchange, and calcination conditions. Their high thermal stability permits them to be used at high temperatures that often result in higher yields and easier heat recovery. All of these characteristics, and especially the control of structure and acidity, make zeolites well suited as catalysts for organic reactions [49,50,51]. Traditionally, zeolites aluminosilicates) are defined as crystalline materials in which Si and Al are tetrahedrally coordinated by oxygen atoms in a three-dimensional network creating uniform sized pores of molecular dimensions.

Furthermore, zeolites have been proven effective as catalysts in many refining and hydroprocessing processes [42]. These reactions have been postulated to proceed through intermediate compounds called carbenium ions which are created on the surface of zeolites through interaction of reaction molecules with active sites. Zeolites then act as ‘‘solid acids’’ which are capable of converting the adsorbed molecule into various forms. This is accomplished by either transforming a proton from the solid acid to the adsorbed molecule (Bronsted acid site) or by transferring

electron pairs from the adsorbed molecule to the solid surface (Lewis acid site). Zeolite acidity arises from the imbalance in charge between silicon and aluminum atoms within the framework so that each aluminum atom is capable of inducing a potential active site.

The following main characteristics of the zeolites have contributed significantly to the commercial success of zeolites:

- High surface area and adsorption capacity.
- Active sites, for example acid sites can be generated in the framework and their strength and concentration can be tailored for a particular application.
- The sizes of their channels and cavities match with the dimensions of most of the molecules involved in various chemical processes (i.e. 0.55–1.2 nm)
- The complex channel structure in the zeolites allows different kinds of shape selectivities, i.e. product, reactant, and transition state.

As the number of zeolite structures increased and as the basic knowledge of zeolite acidity and shape selectivity grew, it became evident that, the molecular sieves would play a vital role in organic synthesis. The pores of zeolites are similar in size to small organics and have shown the ability to recognize, discriminate and organize molecules with precisions that can be less than 1 Å [48,52]. Weisz et al. have reported shape-selective, acid catalysis using a zeolite catalyst for the first time [53]. The reason behind the success of zeolites as commercial catalysts is its ability to control the catalytic properties by a variety of synthetic and post-synthetic methods. By choosing the appropriate organic template and synthesis conditions, the pore size and pore shape (dimensionality, intersections, and cages) may be directly influenced. The acidity of the zeolite may also be controlled through various methods such as silicon/aluminium (Si/Al) ratio, ion exchange, and calcination conditions. Their high thermal stability permits them to be used at high temperatures that often result in higher yields and easier heat recovery. All of these characteristics, and especially the control of structure and acidity, make zeolites well suited as catalysts for organic transformations.

4.1.2. H-ZSM-5 catalyst

Among the different zeolites, ZSM-5 (Zeolite Socony Mobil-5) is a very stable zeolite with a variable content of alumina and has pores of 5.5 Å diameter. It is widely used in hydroprocessing due to its unique structure. The relatively small size of the pores allow only narrow (~4 Å dia) molecules enter its pores and undergo rapid hydrogenolysis [52]. The framework type of the high silica zeolite ZSM-5 can be described in terms of pentasil units (one honeycomb-shaped ring in Fig. 1a) [53]. These units are linked to form pentasil chains, and mirror images of these chains are connected via oxygen bridges to form a 3-dimensional structure. The overall structure can be viewed in Fig. 1b.

4.1.3. Other zeolites of interests and recent advances

HZMS-5 is only one example of a widely used zeolite. It exhibits smaller pore diameter as it has 10-member-ring (MR) openings and thus is ideal for processing of petroleum products. Nonetheless, bio-oil contains many bulky molecules with side chains. Therefore, other zeolites with large ring openings should be considered. Y zeolites have a 12 MR and have been proven to be an effective catalyst in hydrodesulphurization. They are commonly used as fluid catalytic cracking (FCC) catalysts as a part of a diluted framework [14]. For carrying out various kinds of organic transformations, zeolite catalysts of different acid strengths and textural properties are required. A study concerning the transformation of a model bio-oil ketone, the cyclopentanone, over two HY zeolites presenting different acidities, demonstrated that the ketones reactivity highly depends on the nature of the zeolite acidity at lower temperatures, on the zeolites with lower acid strength, higher Brönsted acid site density and larger concentration of extra framework aluminum species than over the zeolites with higher acid strength but lower acid site density [55].

Zeolite beta is promising due to its optimal pore dimensions and higher surface area. Furthermore, beta-zeolites (a 12 MR zeolite) were most commonly used in hydrocracking reactions before Mobil's discovery of pentasil zeolites (ZSMs). Catalytic upgrading of bio-oils was tested by several authors, in a temperature range of 290–450 °C [3,56–58]. Lopes et al. have indicated that the bio-oil can be upgraded over zeolites [59]. They found the HZSM-5 zeolite as the best catalyst amongst HMOR, HY, silicalite, and silica–alumina, with the highest production of liquid products and low coke deposition. In fact, a higher deoxygenation rate was achieved with the HZSM-5 zeolite. HZSM-5 and HMOR catalysts produced more aromatic hydrocarbons. They further concluded that, HZSM-5 is useful to produce hydrocarbons in the gasoline range whereas in the kerosene boiling point range, HY and HMOR are preferable. They suggested that, by changing the type of catalyst, it is possible to tailor-make composition of the organic distillate fraction resulting from bio-oils deoxygenation. Recent review [3] reveals trends in the chemistry of bio-oil upgrading processes for biofuel production and the catalysts used.

According to Guo et al. [60], mesoporous materials having strong acid sites in combination with large pore dimensions would be beneficial as promising catalytic materials. Such materials prevent pore blocking by macromolecules present in the bio-oil and thus, avoid catalyst deactivation during upgrading process.

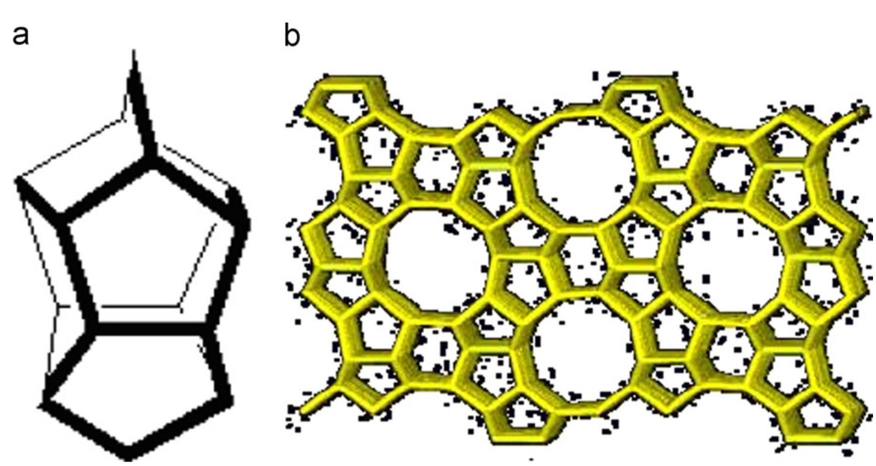


Fig. 1. (a) Pentasil Unit [3] and (b) ZSM-5 structure [55].

Use of mesoporous materials having pore openings higher than 2 nm, in some of these processes has not succeeded due to their low hydrothermal stability [61]. Thus, selection of suitable catalysts is extremely important in any bio-oil upgrading process. In case of bio-oil upgrading process, which involve use of bulky reactants products, certain limitations are associated with use of zeolite in terms of restricted pore size (<1 nm) which may induce some diffusion problems [62].

The ability of reducing mass transfer limitations together with high active site accessibility increases the catalytic potential of zeolites. Therefore, there is need to improve pore accessibility of zeolites. This can be achieved as reported by Moliner [63], either by synthesizing well-structured microporous materials with larger pores, or by creating secondary mesoporous systems within the microporous zeolitic matrix. In this context, preferred way is the preparation of hierarchical materials containing micro- and mesoporosity, by simple post synthetic modifications (for e.g. dealumination and desilication). The double templating route is also extensively reported for the synthesis of hierarchical zeolites. Choi et al. [64] have applied new hierarchical zeolites as attractive catalysts in various industrially relevant chemical processes. The strong acidity of zeolite together with large intracrystalline void volume, offered unique catalytic properties in reactions involving large molecules or avoiding catalyst deactivation by coke deposition. The retardation of catalyst deactivation in different catalytic processes, such as cumene cracking, isomerization or esterification has been reported. Another reported route to expand the pore is addition of triblock copolymers as co-pore-expanding agents. The mesoporous LTA prepared by this route, having expanded pore (to 24 nm), showed excellent catalytic properties for the conversion of methanol to dimethyl ether and hydrocarbons. Also these authors have observed enhanced product selectivities, catalytic activity and lifetime. Other routes for the direct preparation of a hierarchical micro-mesoporous zeolite include, combining organic and inorganic directing effects [65], and the direct OSDA-free synthesis of ultra-small EMT zeolite by capturing methods [66]. OSDA-free synthesis is a very challenging area and is of great interest to the industry as organic molecules used as templates increase the overall cost of the synthetic procedure. Seeding methodology as a substitute to OSDA-free synthesis, have allowed the preparation of different zeolitic materials used in the industry without organic templates. Xie et al. [67] have tested the catalytic activity of OSDA-free beta zeolite in the catalytic cracking of a real industrial feedstock (Fushum light vacuum gas oil) and observed much higher activity for OSDA-free beta than regular beta and Y zeolite. Also, they obtained the highest yield of LPG, and at the same time, the lowest yield of heavy oil using OSDA-free beta zeolite.

The functionality of zeolites can be changed by incorporating the metals via post synthesis modification. Although the catalytic activity is heavily dependent on the kind of zeolite and its SiO_2/Al_2O_3 ratio, addition of metal promotes additional functionality in the hydrogenation and deoxygenation reactions. The direct synthesis of metal-containing, both in framework and extra-framework positions, of new zeolitic structures with isolated metals, or small-metallic clusters, is fast growing area of research, as this direct route offers extraordinary opportunities to control the location of the metallic active sites in the final solid and reduction in synthesis step count making eye catching methodology for the industry. In recent times exciting challenges have been emerged in the direct synthesis of new functional metal zeolites in view of recent applications of metal–zeolites in biomass derived processes [63].

4.2. Metal supported catalysts for hydrotreating

Metals from group VIII, such as nickel, are well known for their hydrogenation activity and usefulness in hydrotreating processes. The hydrogenation activity of the group VIII metals increases across the transition series in the order of Fe < Co < Ni [68]. Thus, nickel, palladium, and platinum have the highest hydrogenation activity of group VIII metals. Furthermore, nickel and platinum make ideal catalyst as they adsorb reactants strongly enough and activate them, at the same time it is not that much strong which can make product desorption difficult [68]. Nonetheless, nickel is more abundant and less expensive than palladium and platinum.

Group VIB metals, such as tungsten and molybdenum, have also been proven effective in hydrotreating processes and may prove to be effective in oxygen removal. Tungsten is a well-known hydrotreating catalyst and in some studies has proven more effective than molybdenum [69]. Tungsten is highly effective in HDN and HDS, thus it should also be active in HDO. Furthermore, elemental tungsten resists attack by oxygen, acids, and alkalis makes it a promising catalyst for the resistance of poisoning from water present in bio-oil, organic acids, and high level of oxygenates [69]. W/ZSM-5 has proven as an effective catalyst in the conversion of oxygenates through the MTG (methanol to gasoline) process wherein, only 3.2 wt% tungsten was capable of an optimum methane conversion of 29.4% corresponding to C_5+ selectivity of 57.2% [70].

Sr-ZSM-5 was explored in a study by Okado et al. [71] where the authors tested Mg, Ca, and Sr containing ZSM-5-type zeolite for oxygenate-to-gasoline reactions. It was found that, all modified zeolites had increased selectivity to olefins at temperature above 500 °C [54]. In a long term testing of ZSM-5 containing alkaline earth metals, the strontium containing zeolite showed the most stable activity [68].

Furthermore, commercial hydrotreating catalysts such as NiMo and CoMo have been proven effective not only in conventional petroleum hydrotreating, but also in the hydrotreatment of bio-oil [7,72–74]. However, these metals have normally been studied on a γ-alumina support. Alumina has a tendency to interact with transition metals which, in turn, lowers the life of the catalyst whereas zeolite is a thermally stable, robust support. Thus, CoMo and NiMo on ZSM-5 will display multi-functional characteristics. Acidic, hydrophobic and high activity functions of the support will help to crack and hydrogenate large molecules in the bio-oil while the noble metals assist oxygen removal.

Stability of catalyst is a critical parameter to be considered while designing a catalyst. Most catalysts show decrease in the activity with time. This can be attributed to the partial blocking of active edges of MoS_2, Mo_2C and Mo_2N catalysts or formation of carbonaceous deposits on the catalyst surface leading to fouling [75]. Generally, deactivation rate is higher for catalyst with higher acidity [76]. Blockage of pores by deposits also hinders the activity. Almost in all the works, tremendous losses of surface area and pore volume have been reported for spent catalyst in comparison to fresh catalyst. From the conclusions reported by Rodriguez [77], it can be seen that, the Ni–S interaction has detrimental effect on the reactivity of nickel and hence, similar trend can be assumed for hydrodeoxygenation systems wherein Ni–O interactions should be minimized. C–C bond cleavage occurs on active metal sites while C–O bond cleavage occurs on acid sites by dehydration reactions [78].

5. Model compound upgrading

Because of the complicated nature of bio-oil, many researchers have chosen to work with model compounds or synthetic bio-oil to develop successful techniques in upgrading. Because most bio-oils are highly phenolic in nature, a large amount of research in this area has concentrated on deoxygenation of phenols.

5.1. Upgrading phenols at high pressure

Senol et al. [79] carried out a thorough investigation on HDO of phenol using stainless steel tubular flow reactor. 1–3 mm of either commercial NiMo/γ-Al_2O_3 or CoMo/γ-Al_2O_3 was packed between two layers of silicon carbide and activated at 400 °C under atmospheric pressure. Experiments were carried out at 250 °C under 15 bar with H_2S/H_2 mixture.

Reaction products of phenol detected in the liquid samples included aromatic and alicyclic hydrocarbons and a few oxygen-containing compounds. The HDO products of phenol were benzene, cyclohexane and cyclohexene, while oxygen-containing compounds were cyclohexanone and diphenyl ether. In addition, due to the presence of H_2S, a sulphur containing compound, cyclohexanethiol, was detected. The oxygen- and sulphur- containing compounds were formed in trace amount.

In their study, Senol et al. [79] explored the effect of H_2S on the reactions with phenol. HDO conversion of phenol was found 19% and 28%, respectively, using NiMO and CoMo catalyst, without H_2S addition. However, with 60 ppm H_2S addition, the conversion dropped to 16% and 20% for NiMo and CoMo, respectively. Similar decreasing trend continued with higher amount of H_2S addition, beyond 60 ppm. They compared HDO of phenol and aliphatic oxygen-containing compounds and found noticeably higher HDO conversion for the phenol and aliphatic oxygenates, in both cases, absence and presence of sulphiding agent. They found NiMO catalyst more preferable for the HDO of the methyl ester than is CoMo catalyst, in both cases, with and without H_2S addition. However, in case of phenol HDO the situation found reverse, showing difference in catalyst activities for the HDO of aromatic and aliphatic oxygenates. Sulphur anion vacancies mentioned as catalytic site for cleavage of oxygen from the aliphatic oxygenates [80]. They suggested that, as same site is responsible for direct hydrogenolysis reactions, H_2S could be expected to have similar effects on the HDO of phenol and the aliphatic oxygenates. They explained the cause for different effects of the sulphiding agent on the HDO of aromatic and aliphatic oxygenates in a way that, HDO of the aliphatic ester, alcohol, and carboxylic acid compounds mainly occurs through hydrogenation reactions and acid-catalyzed reactions (hydrolysis, dehydration, esterification, E_2 elimination and SN_2 nucleophilic substitution) and concluded based on effects of H_2S that, Bronsted acid sites are vital for the acid catalyzed reactions. Further, they mentioned based on several reports [81–83] that, the dissociative adsorption of H_2S on sulphided catalysts increase the acidity of the catalyst. Correspondingly, the promoting effect of H_2S was attributed to the increased catalyst acidity in the presence of H_2S [80].

The hydrocarbon formation through direct hydrogenolysis reaction in the HDO of phenol was suggested more directly related to availability of the vacancy sites and not to catalyst activity. This consequently leads to different reaction mechanisms, which are essentially influenced by the molecular and electron structures of aromatic and aliphatic oxygenates, resulted in divergent effects of the sulphiding agent on the HDO of the aromatic and aliphatic oxygenates, In the HDO of aliphatic oxygenates, H_2S addition showed suppressing effect on the hydrogenation reactions on the NiMo catalyst whereas not to affect them on the CoMo catalysts [80]. Thus, the hydrogenation reactions were affected similarly in the HDO of phenol and aliphatic oxygenates.

The formation of sulphur-containing compounds in the feed was reported even in the absence of sulphiding agents and were discovered in the HDO of aliphatic oxygenates [84]. This observation suggested a possibility of key role of reactive sulphur species on the catalysts in the formation of sulphur-containing compounds. In contrast, in the HDO of phenol, a sulphur-containing compound was detected only when sulphiding agent was added to the reactor. They finally concluded that, the composition of the bio-oil feed is key responsible parameter for the performance of the HDO process and the effect of the sulphiding agent added to the HDO feed to maintain catalyst activity and stability. Addition of sulphiding agent to a wood-based HDO feed containing mainly phenolic compounds, will probably affect the total HDO negatively. In contrast, a promoting effect is likely for vegetable oils and animal fats, which mainly involve aliphatic oxygenates.

Elliot [85] at the Pacific Northwest National Laboratory (PNNL) did extensive work on heterogeneous catalytic processing of bio-oil. Initial work involved batch reactor tests of model phenolic compounds with various catalysts. Commercial samples of catalysts (CoMo, NiMo, NiW, Ni, Co, Pd, and CuCrO) were used to hydrogenate phenol at 300 °C or 400 °C and 140 bar (1 h at temperature). Of the catalysts tested, the sulphided form of CoMo was the most active producing a product containing 33.8% benzene and 3.6% cyclohexane at 400 °C. The Ni catalyst was also active, producing a product with 16.9% benzene and 7.6% cyclohexane at 400 °C. A Pd catalyst produced a 7.8% benzene product with 2.7% cyclohexane but 5.5% cyclohexanone. At a lower temperature of 300 °C, cyclohexanone was the primary product at 8.1% and benzene and cyclohexane were nearly equal at 2.0% and 2.5%, respectively.

In 2008, Yang et al. [86] published work investigating hydrodeoxygenation of crude bio-oil using phenol as a model compound in supercritical hexane. Reactions were carried out at temperature of 300–450 °C and hydrogen pressure of 5 MPa with MgO-supported sulphided CoMo with and without phosphorus as a catalyst promoter (CoMoP and CoMo). In this study, it was concluded that, both MgO-supported catalysts proved to be effective for HDO of phenol in supercritical hexane at temperatures greater than 350 °C. The HDO activity of the catalyst was greatly promoted by addition of a small amount of phosphorus. Further, the HDO of phenol may proceed with direct hydrogenolysis reaction and hydrogenation reaction involving cyclohexanol as an intermediate/precursor, resulting in conversion of phenol into benzene, cyclohexyl-aromatics and C_{12}-products. Hydrogenolysis of phenol to benzene (direct elimination of the hydroxyl group) is the dominant reaction and it becomes much more favorable at a higher temperature.

The HDO activity of CoMoP/MgO increased drastically with increasing the reaction temperature. The hydrotreatment of phenol at 450 °C with CoMoP/MgO catalyst led to a liquid product containing 10.2% phenol and 64% benzene. Furthermore, very little coke formation was detected. This superior resistance to coke formation was attributed to the basic character of the MgO support.

Kallury and Tidwell [87] explored HDO of phenol over MoO_3–NiO–Al_2O_3 catalyst in an autoclave batch reactor at a temperature of 350–450 °C and pressure of 2.8–9.8 MPa. The reaction of phenol using the MoO_3–NiO catalyst at 450 °C and 2.8 MPa gave essentially complete conversion of the reactant after 45 min reaction time, with formation of benzene (60%), cyclohexane (16%), and methylcyclopentane (7%) as the major products. In addition, a group of products were formed that were presumably derived from coupling of two phenol-derived units, namely, cyclohexylcyclohexane (2%), diphenyl (3%), and cyclohexylbenzene (2%). These results indicate that benzene is essentially inert to these reaction conditions.

At lower temperatures of 350 °C or 400 °C, the conversion of phenol is not complete even after 2 h, and the proportion of saturated products had increased at the expense of the benzene. Evidently the reaction mechanism for the hydrogenolysis of phenol to benzene and the ring saturation to cyclohexanol are quite different, and the former process becomes much more favorable at higher temperatures.

Fisk et al. [88] explored model compound upgrading through a synthetic bio-oil. The oil consisted of a mixture of methanol (5 wt%), acetaldehyde (12 wt%), acetic acid (14 wt%), glyoxal (4 wt%), acetol (8 wt%), glucose (8 wt%), guaiacol (17 wt%), furfural (4 wt%), vanillin (8 wt%), and de-ionized water (20 wt%). Upgrading of the synthetic oil was carried out in a stainless steel autoclave at 0.7 MPa and 350 °C over a series of supported Pt catalysts. Of the catalysts tested, Pt/Al_2O_3 showed the highest activity for oxygen removal, the oxygen content of the model oil decreasing from an initial value of 41.4 wt% to 2.8 wt% after upgrading. Analysis of the product oil showed it to be highly aromatic, the major components corresponding to alkyl-substituted benzenes and alkylcyclohexanes. CO_2 was formed as the major gaseous product, together with lower yields of H_2 and C_1–C_6 hydrocarbons.

Based on the products obtained in these experiments, bio-oil upgrading is suggested to proceed via two main pathways. The first of these corresponds to reforming of the light oxygenates, resulting in H_2 generation and O_2 rejection as CO_2. Simultaneously, the aromatics present undergo C–O bond cleavage; in the presence of H_2, this leads to the formation of benzenes and their hydrogenated products. The highly alkylated nature of the products appears to be a consequence of the acidic nature of the reaction medium, favoring the occurrence of aromatic electrophillic substitution reactions. The formation of coke was also observed, believed to be due to both thermal and catalyzed reactions. This suggests that for prolonged operation, regular burn-off of the coke would be necessary to maintain the catalyst in an active state.

Table 7 presents a summary of model compound upgrading that has been completed via hydrotreating over the past few decades. All studies examined oxygen removal through hydrodeoxygenation using moderate to high temperatures and pressures as well as a traditional hydroprocessing metal catalyst such as CoMo, NiMo or Pt on alumina. In all cases, benzene and cyclohexane were the main products.

5.1.1. Reaction mechanism

Another notable discovery made through model compound studies was the prediction of reaction mechanisms. Hydrodeoxygenation (HDO) can be defined as the removal of the heteroatom, oxygen, in the form of water in the presence of hydrogen. More specifically, HDO of phenolic compounds proceeds through hydrogenolysis and hydrogenation reactions [86]. Hydrogenolysis removes the oxygen yielding a benzene ring; then, subsequent hydrogenation yields cyclohexene and cyclohexane. However, it is possible for the reaction to proceed primarily through hydrogenation of the aromatic ring to yield cyclohexanol with subsequent hydrogenolysis to rapidly dehydrate the alcohol to yield cyclohexane [86]. Fig. 2 depicts these proposed pathways. HDO products of phenol are commonly benzene, cyclohexane and cyclohexene. This mechanism was proposed by both Satterfield [3] and Senol et al. [79].

Kallury et al. [87] presented an alternative reaction where a group of products (C_{12} products) were formed. These were presumably derived from the coupling of two phenol-derived units, namely, cyclohexenecyclohexane, cyclohexenebenzene, and diphenyl. This alternative is presented in Fig. 3. It should be noted that, $NiMo/Al_2O_3$ promotes hydrogenolysis (the upper pathway in Fig. 3) over Co, where $CoMo/Al_2O_3$ promotes hydrogenation (the lower pathways in Fig. 3) over Ni. This suggests that the metal provides acid sites that are shared by both reaction pathways. A bifunctional catalyst that provides separate sites for both reactions is desired.

5.2. Upgrading phenols and bio-oil at low pressure with zeolites

Adjaye et al. [42] utilized a fixed-bed reactor at a temperature of 330 °C, atmospheric pressure, and 3.6 WHSV. HZSM-5 activity was explored on a mixture of model compounds representing bio-oil [propanoic acid, methyl ester of acetic acid, 4-methylcyclohexanol, cyclopentanone, 2-methylcyclopentanone, methoxybenzene, ethoxybenzene, phenol and 2-methoxy-4-(2-propenyl)phenol]. The mixture of model compounds contained 14.6 wt% phenol which produced 5.1% conversion to benzene. Their low phenol conversions were contributed to phenol's stable nature. It was predicted that, isomerization of the original molecule was the main reaction route in their studies.

Sharma and Bakshi [89] used a fixed bed reactor and tetralin as a hydrogen-donor solvent to upgrade oil produced by the Waterloo fast pyrolysis process. About 66 wt% conversion of the non-volatile matter, a maximum of 60 wt% organic liquid product and coke fractions between 11 wt% and 17 wt% were obtained.

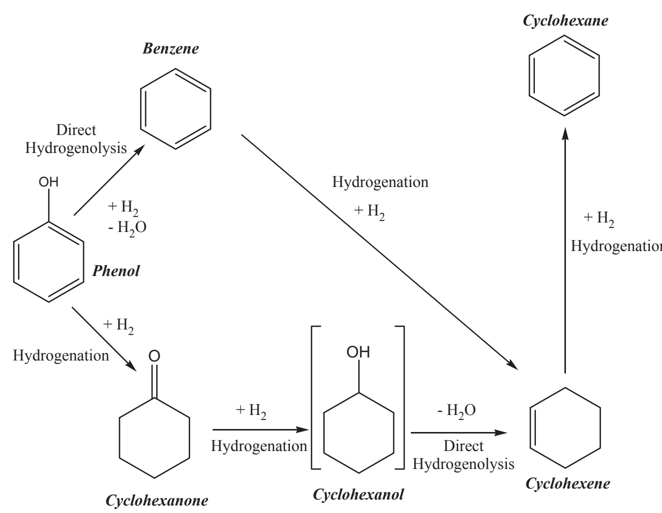


Fig. 2. Reaction scheme for the HDO of phenol on sulphided catalysts [68].

Table 7
Summarization of model compound upgrading via hydrotreating.

Ref.	Feedstock	Diluent	Catalyst	T (°C)	P (MPa)	Conversion[a] (%)	Reaction system
Senol et al., [78]	Phenol	m-xylene	$CoMo/Al_2O_3$	250	1.5	28	Fixed-bed
Elliot, [85]	Phenol	n-octane	$CoMo/Al_2O_3$	400	14	34	Batch
Yang et al., [86]	Phenol	n-hexane	CoMo/MgO	380	5.0	51	Batch
Kallury and Tidwell [87]	Phenol	n-octane	$NiMo/Al_2O_3$	450	2.8	60	Batch
Fisk et al., [88]	Synthetic bio-oil[b]	–	Pt/Al_2O_3	350	0.7	60	Batch

[a] HDO Conversion (%).
[b] A mixture containing methanol (5 wt%), acetaldehyde (12 wt%), acetic acid (14 wt%), glyoxal (4 wt%), acetol (8 wt%), glucose (8 wt%), guaiacol (17 wt%), furfural (4 wt%), vanillin (8 wt%), de-ionized water (20 wt%).

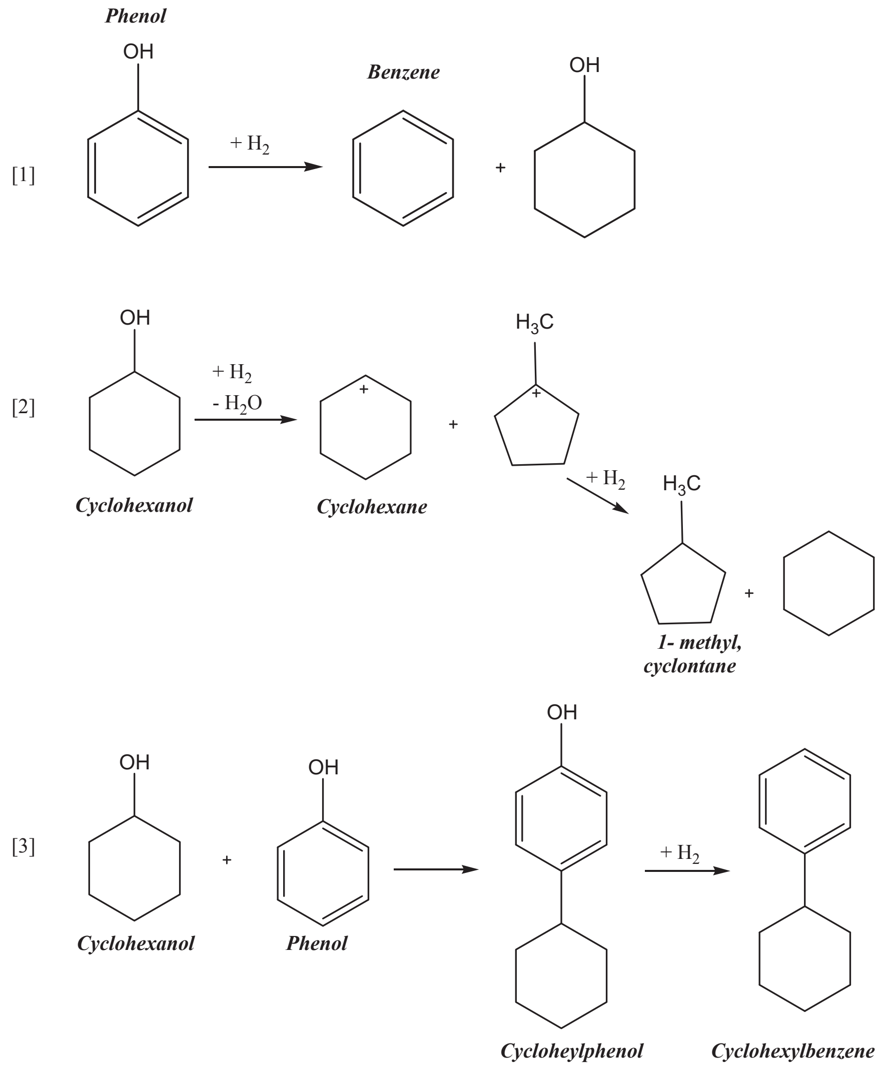


Fig. 3. Reaction scheme for the hydrodeoxygenation of phenol as proposed by Kallury and Tidwell [87].

Chen et al. [90] achieved 68 wt% conversion of a pyrolytic oil using helium as a carrier gas in a fluidized bed. Upon processing with methanol as a co-feed in a 1:1 weight ratio, the conversion increased to 85 wt%. Also, the methanol resulted in reduced coke formation from 9 wt% to 4 wt%. However, they obtained very low yields of hydrocarbons (6 wt% in the absence of methanol, and 11 wt% with methanol) probably due to the high flow rates (850 mL/min) employed.

Gayubo et al. [91] explored bio-oil upgrading at atmospheric pressure in a "two-step" process. Crude bio-oil was continuously fed through a u-shaped reactor which can be viewed in Fig. 4. The first part of the "u", the feed preheating zone, is filled with glass spheres where the carbonaceous matter produced by polymerization of bio-oil lignin derivates is deposited. This is thought to attenuate the catalyst life and reduce coking drastically. The second part constitutes actual reaction wherein, the catalyst is placed on a glass wool layer, which is supported by the bed of glass spheres. Typical reactions were carried out at 400 °C, feed rate of 0.20 cm^3/min., and a reaction time of 1 h. It was observed that at temperatures above 400 °C, there was only a minimal increase of lignin deposition on the glass beads.

Furthermore, Gayubo et al. [91] observed that, water addition treatments and dilution of bio-oil with methanol considerably reduce pyrolytic lignin deposition. In the case of water addition treatments, this beneficial effect is due to both dilution and

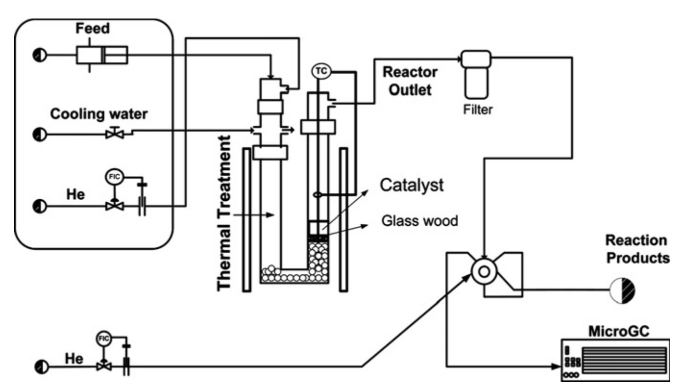


Fig. 4. Reaction equipment utilized for "two-step" upgrading by Gayubo et al. [91].

composition, given that they slightly decrease the proportion of problematic compounds, such as phenols, in the aqueous fraction obtained subsequent to treatment with water. Methanol co-feeding attenuates the thermal degradation of bio-oil and this result is not only due to dilution. It is observed that, as methanol content in the mixture is increased, there is a steady and almost linear decrease in the percentage of bio-oil degraded. For methanol contents in the feed higher than 70 wt%, the fraction of bio-oil deposited is constant. This result indicates that, methanol

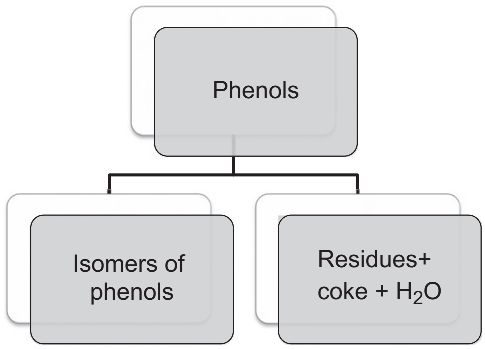


Fig. 5. Reaction pathway for the conversion of phenols [42].

addition has a beneficial effect not only due to feed dilution but it also inhibits the reactions of condensation of bio-oil phenolic components.

Methanol co-feeding by 70 wt% with crude bio-oil gives way to the maximum attenuation of pyrolytic lignin deposition and a considerable decrease in catalyst deactivation, with an initial bio-oil conversion similar to that achieved by feeding crude bio-oil. With a moderate space-time and temperature above 400 °C, the conversion of the bio-oil in the mixture is higher than 92 wt%, with a hydrocarbon yield higher than 80 wt%.

5.2.1. Reaction mechanism

When using a zeolite to upgrade bio-oil, phenol, or other oxygenates under atmospheric pressure the reaction is hydrogen limited [92]. Zeolites are known to deoxygenate through carboxylation and dehydration [42]. As mentioned earlier, Adjaye et al. [42] examined phenol and substituted phenols under the conditions previously stated. As mentioned above, the major products were the isomer of the phenol showing that isomerization of the original molecule was the main reaction route. Isomerizations of substituted phenols have been mentioned to be one of the major reactions over zeolite catalysts [93,94].

The second reaction route occurring to a far lesser extent involves condensation-type reactions, which resulted in aqueous fraction and high boiling molecules, mainly ethers. It has been mentioned [95] that, the dehydration of phenol leads to an intermediate ether formation. Successive condensation may result in non-volatile residue or coking. This intermediate could be the cause of the severe coking and reactor plugging that occurs with the lignin-rich bio-oil fractions when upgrading at high temperatures. The proposed pathway for upgrading phenol over ZSM-5 at atmospheric pressure is given in Fig. 5.

A notable conclusion from Adjaye's thesis work was how effectively ZSM-5 converted ethers and ketones even though its conversion of phenol and its derivatives were low under the same conditions. This occurred because ethers as well as ketones are less stable than phenols and can give up oxygen more easily by forming or breaking double bonds where the oxygen was attached. This is not possible with phenol as the attached benzene ring is completely stable. Ethers (furans) and ketones (cyclopentanone, etc.) are abundant in bio-oil and must be deoxygenated in order to obtain a quality product. Therefore, these reactions are also important and make upgrading bio-oil via ZSM-5 more appealing.

6. Hydrotreatment of bio-oil to obtain chemicals and fuels

Bio-oil is disadvantageous as a fuel in its crude form mainly due to its high oxygen content. This contributes to negative attributes such as: high viscosity, instability, corrosiveness, and a low heating value. Therefore, it is essential to upgrade the bio-oil in order to reduce/remove the oxygen. This can be accomplished through hydrodeoxygenation. If the bio-oil is mostly phenolic (which typical pyrolysis oil is), then HDO can proceed through the reaction mechanism proposed in Figs. 3 and 4 as the model compound studies would accurately represent the true feedstock.

6.1. Common problems with polymerization

The most common obstacle when utilizing either hydrodeoxygenation/catalytic cracking as the upgrading method is that, the yield of desirable upgraded oils is generally low because of the high yields of char, coke and tar [10]. The coking can be so severe that, it plugs fixed-bed reactor systems resulting in termination of experimentation [16]. Co-feeding hydrogen donors as well as utilizing a two-step reaction procedure can increase desirable product yield while decreasing the undesirable carbon deposition. The most common co-feeds are methanol, tetralin, and decalin. The hydrogen donor not only promotes cracking and hydrogenation reactions but also serves to dilute the lignin and decrease polymerization at high reaction temperatures.

6.2. Successful upgrading of bio-oil via hydrotreatment

Soltes et al. [96] conducted studies on the hydroprocessing of tars produced from the pyrolysis of biomass (a very phenolic substance). The tests were carried out under hydrotreating conditions (high pressure and temperature) in a batch reactor with decalin as a hydrogen donor. Various catalysts were screened and hydrocarbon conversion varied from 56% on a Pd/alumina catalyst to 3% on silica–alumina.

Zhang et al. [97] studied bio-oil upgrading into liquid fuel by hydrotreatment using sulphided CoMo-P/Al_2O_3, in an autoclave, with tetralin as a solvent. The optimum conditions were, temperature: 360 °C, reaction time: 30 min., and a cold hydrogen pressure of 2 MPa. These optimum conditions yielded 75.8% conversion with 59.6 wt% hydrocarbon-rich product. The density and oxygen content of the bio-oil were found to decrease. The heating value, 41.4 MJ/kg of upgraded oil was doubled as compared to 21.3 MJ/kg of raw bio-oil, as a result of oxygen removal.

Baldauf et al. [98] studied the hydrotreatment of bio-oil both in a thermal and catalytic mode in a fixed-bed reactor over hydrotreating catalysts, CoMo/Al_2O_3 and NiMo/Al_2O_3 at 350 °C and 18 MPa. Thermal hydrotreatment resulted in 70–80 wt% reductions in oxygen content in the final product whereas $>90\%$ deoxygenation was achieved when using catalysts. Depending on the severity and the water content of the feedstock, a product yield of 30–50% could be achieved. The product was fractionated by distillation and it was shown that, the product properties of the heavy fraction are close to those of a FCC feedstock. The light fraction had properties close to that of gasoline.

Churin et al. [99] used a fixed bed reactor loaded with CoMo and NiMo catalysts for upgrading of pyrolysis oil. Upgrading was carried out in the presence of hydrogen at 5–12 MPa and 270–400 °C. The oil initially contained 10–20 wt% hydrocarbons and 40 wt% phenols. After upgrading the hydrocarbon fraction increased to 70 wt% while the phenols decreased to 18 wt%. In the presence of tetralin, the fraction increased further to 75 wt% and 20 wt%, respectively. However, the role of tetralin or its recovery was not studied.

Baker and Elliot [16] upgraded bio-oil through hydrogenation, a fast pyrolysis oil produced at Georgia Tech. Upgrading was carried out in a reactor with two temperature stages using CoMo/Al_2O_3 catalyst, at 13 MPa. The first and second zones were maintained at 274 °C and 353 °C, respectively. The yield of hydrocarbons was

31 wt% of the oil. Rapid catalyst coking was also observed and was considered a major problem.

Oasmaa and Czernik [34] studied bio-oil upgrading via batch-wise hydrotreatment at 21.5 MPa, 390 °C, reaction time of 2 h and a catalyst loading of 10 wt%. The catalyst explored was 4% CoO/15.5% MoO_3/Al_2O_3. Through this procedure, oxygen content was lowered from 22% to 3%. Nitrogen and sulfur contents of the product were 4.3% and 0.10%, respectively. Straight-chain material predominated in the upgraded product and C_{14}–C_{29} *n*-alkanes have been identified along with some phenols.

Wildschut [2] carried out a catalyst screening study using noble metal catalysts for the hydrotreatment of fast pyrolysis oil. The reactions were carried out in an autoclave batch reactor at two conditions relevant for the process, a mild hydrotreatment at 250 °C (100 bar hydrogen) and a more severe hydrotreatment at 350 °C (200 bar hydrogen). Distinct differences in catalyst performance, product yield and product properties were observed for mild and deep hydrotreatment. Ru/C catalyst was found superior.

Using Ru/C catalyst, in mild HDO conditions, product oil obtained in yields between 21 wt% and 55 wt% (dry basis), with an oxygen content between 18 wt% and 27 wt%, respectively. The yields as well as the level of deoxygenation for the noble metal catalysts were higher than for the classical hydrotreatment catalysts. At deep HDO conditions, two liquid products were obtained corresponding to two noble catalysts, one with a density higher and the other with a density lower than water.

The composition of the top oil differs from that of the bottom oil and the top oil has a higher H/C and O/C ratio. The weight average oxygen level of the product oils was between 5 wt% and 11 wt%, which is considerably lower than for the mild HDO process.

Relevant product properties and the chemical composition of the top oil produced at deep HDO conditions (350 °C, 200 bar, 4 h) using the Ru/C catalyst were determined. The heating value is about 43 MJ/kg which is considerably higher than for the feed pyrolysis oil (20 MJ/kg). The acidity of the hydrotreated oil is considerably lower than the original feed as expressed by an increase in the pH from 2.5 to 5.8.

Mahfud et al. [100] conducted an experimental study on the hydrodeoxygenation of pyrolysis oil using heterogeneous catalysts with the objective to produce oil with product properties in the range of conventional liquid transportation fuels. Catalyst screening studies were carried out at temperatures up to 350–425 °C. Mahfud concluded that, amongst the classical hydrotreating catalysts, pre-sulphided NiMo on alumina is a more active catalyst than pre-sulphided CoMo on alumina and Ru on alumina. These results indicate that no sulphur is required in the feed.

Process studies on the NiMo catalysts indicated that, (i) HDO oil with an oxygen content of 10 wt% could be obtained and (ii) There is a strong indication for excessive catalyst deactivation, either due to the presence of water, the absence of sulphur or pore blocking by char formation. 100 g. of crude pyrolysis was converted to 34 g. of HDO oil, 42 g. of an aqueous phase, 13 g. of gas and about 4 g of char using the NiMo catalyst. The energy efficiency of the process is about 62%. The HDO oil produced with the NiMo catalyst has a heating value of about 39 MJ/kg, which is about twice of that of crude pyrolysis oil.

Jacobson [101] explored the valorization of fast pyrolysis bio-oil from maple sawdust in two steps. Primarily, solvent extraction was carried out to remove water from the bio-oil (35% water, 55% oxygen and a heating value of 21.6 MJ/kg). The solvents explored were benzene, ethanol, and chloroform. Chloroform reduced the amount of high molecular oxygenates from 58% to 30%, increased the amount of hydrocarbons from 20% to 41%, and reduced the moisture content to $<0.2\%$. The modified bio-oil was comprised almost entirely of phenol and phenol derivatives. It possessed 42% oxygen and a heating value of 44.0 MJ/kg. Then, the objective was to remove oxygen while obtaining a high yield of hydrocarbons suitable for use as transportation fuels through hydrodeoxygenation. Hydrodeoxygenation of the modified bio-oil was studied with different metal catalysts impregnated on H-ZSM-5 in a batch reactor. 8.5–13% Mo, 1–5% Ni, 2.5–5% Sr, 5–10% W, CoMo and NiMo were loaded onto H-ZSM-5. The experiments were carried out over a temperature range of 250–350 °C, pressure range of 2–5 MPa, stirring speed of 500 rpm, catalyst loading 2–10 wt%, and a tetralin to oil ratio of 2–10:1. Tetralin was added as a hydrogen donor solvent and lignin dilutant to prevent polymerization of the feed. 2.5% Ni/ZSM-5 proved to be the most effective catalyst with 95% oxygen removal and 89.0% yield of hydrocarbons (20% of which were aliphatic). The least effective was 2.5% Sr/ZSM-5 with 87% oxygen removal and 24.5% hydrocarbon yield. The liquid products obtained via 2.5% Ni had a heating value of 47.0 MJ/kg, a moisture content of 0.07%, and a crystallization point of −81.3 °C. The products were fully miscible with diesel fuel.

Optimization of the process utilizing 2.5% Ni/ZSM-5 catalyst yielded an experimental hydrocarbon yield of 94.3%. The optimum conditions were found to be, temperature: 350 °C, Pressure: 3 MPa, catalyst loading: 3.5 g (7 wt%), solvent to oil ratio: 10, rpm: 500 and a reaction time: 45 min. The liquid products obtained under optimum conditions contained 22 wt% aliphatic hydrocarbons. The physical properties of the liquid product included a high heating value of 47.3 MJ/kg, a low moisture content of 0.07 wt%, a close-to-neutral pH of 6.4, and a crystallization temperature of −88.4 °C. This data reveals potential of such liquid hydrocarbons to be used as a transportation fuel.

A summary of hydrodeoxygenation studies with pyrolysis products to date is presented in Table 8. Two interesting observations can be made from this summary table. The first is the low conversion that Soltes et al. [96] observed when using a metal-free catalyst (SiO_2/Al_2O_3) vs. a Pd catalyst. Without the metal

Table 8
Summary of bio-oil hydrotreating studies.

Reference	Feedstock	Catalysts	*T* (°C)	P (MPa)	Percentage Conversion[a]	Reaction system
Soltes et al., [96]	Tars from pyrolysis (phenolic)	Pd/Al_2O_3	400	0.7	56	Batch
Soltes et al., [96]	Tars from pyrolysis (phenolic)	SiO_2/Al_2O_3	400	0.7	5	Batch
Zhang et al., [97]	Oil phase after water separation	$CoMoP/Al_2O_3$	360	0.2	38	Batch
Baldauf and Baldauf [98]	Crude pyrolysis oil	$CoMo/Al_2O_3$ $NiMo/Al_2O_3$	350	1.8	30–50	Fixed bed
Churin et al., [99]	Crude pyrolysis oil	$CoMo/Al_2O_3$ $NiMo/Al_2O_3$	350	1.2	64–70	Batch
Baker and Elliot [16]	Crude pyrolysis oil	$CoMo/Al_2O_3$	353	1.3	31	Fixed bed
Oasmaa and Czernik [34]	Crude pyrolysis oil	$CoMo/Al_2O_3$	390	2.2	N.R.	Batch
Wildshut [2]	Crude pyrolysis oil	Ru/C	350	2.0	55	Batch
Mahfud [100]	Crude pyrolysis oil	$NiMo/Al_2O_3$	400	2.0	40	Batch
Jaconson [101]	Modified pyrolysis oil	Various[b]	350	3.0	80–95	Batch

[a] HDO Conversion (%); N.R.—Not Reported.
[b] Catalysts explored include 8.5–13% Mo, 1–5% Ni, 2.5–5% Sr, 5–10% W, CoMo and NiMo on H-ZSM-5.

present, conversion was as low as 5% whereas, with palladium present, conversion reached 56%. The second is that a batch reactor seems to yield a higher conversion. This could be due to excessive polymerization in the lines of a continuous system. In all cases, hydrocarbons were the main products.

6.3. Hydrogen donor solvents

Hydrogen donor products are termed liquefaction ''solvents''. These are reactive solvents which act on the hydrogen donor principle: i.e. they are capable of taking up hydrogen easily and can also readily give up hydrogen to form their respective condensed aromatic hydrocarbons [102–103]. Examples of such solvents are tetralin (1,2,3,4-tetrahydronaphthalene), indoline, 1,2,3,4-tetrahydroquinoline.

Hydrogen donor solvents have been used extensively in the processing of coal. In coal liquefaction, this has often resulted in the stabilization of reactive fragments such as free-radicals and in dissolution of such fragments during the initial stages of liquefaction. In the upgrading of coal liquids, hydrogen donor solvents have been used to effect hydrogenation, removal of heteroatoms and reduction in molecular weight [102–104].

The coking and charring of wood–oils in fixed bed operation as a result of low H/C ratios and phenolic nature of the feedstock has been mentioned in the previous sections. Various attempts have been made to process bio-oils with hydrogen donor solvents [89,96,97] with the aim of reducing the coke formation by improving the stability of the oil to temperature effects. In addition, the solvation property of hydrogen donor solvents enhances the effective transport of these feeds, thus, preventing pore blockage which is a problem with feeding of bio-oils into reactors. Increased yields of hydrocarbons have also been observed [90,96,98].

Most processing of bio-oils by hydrotreatment has been carried out in the presence of hydrogen. These processes employ high pressures. The main advantage of using hydrogen donor solvents over hydrogen is the much lower operating pressures that can be employed in its use. In addition, hydrogen donor solvents have better effectiveness in stabilizing the primary thermal decomposition products, thus preventing charring and coking in upgrading work [42], resulting in higher yields for upgraded liquids than hydrogen.

The selection of a solvent can have a profound effect on the yield of liquids products. A number of compounds are available as hydrogen donor solvents as long as they contain mobile carbon–hydrogen bonds [41]. A good solvent readily dehydrogenates and enhances solvation capabilities [102–104]. In addition, it possesses acceptable physical properties such as reasonable viscosity, high liquefaction yields and reduction in char and coke formation are also expected promising criteria to be a good hydrogen donor solvent. Tetralin (1,2,3,4-tetrahydronaphthalene) compared with similar solvents has proven to possess these exceptional properties in both coal and biomass processing to liquid products.

6.4. Product properties

Product properties of HDO oil reported in the literature are scarce, despite the necessity to compare it with crude oil standards. In fact, there is currently no standards are available for the analysis of bio-oils and HDO oils.

The HDO products should fulfill a number of properties before its use as transportation fuel. Products with certain oxygen content may still be attractive biofuels, as oxygen can reduce soot in diesel engines. However, no standards are available yet, in this regard. Properties of particular interest are, elemental analysis (content of O_2, H, C, N, S), water content, heating value, boiling point range, viscosity, organic acid content, solids content, flash points, cold flow properties (pour and cloud point), storage stability etc. These properties may be measured using standardized procedures. Some relations between these properties have been observed. For instance, the viscosity of the product is a function of oxygen content [16]. The high oxygen content oil contains substantial amounts of water, rendering the oil into a relatively low viscosity product (20–50 cps at 20 °C). However, upon oxygen removal, the viscosity increases drastically (up to 100,000 cps at 20 °C). The highest viscosity is observed for oxygen content between 20% and 30%.

Currently, there is a large interest in identification of individual components or classes of components by dedicated analytical techniques. However, this work is seriously hampered by the diversity of components with a broad range of molecular weights in the (upgraded) oils. One technique is often not sufficient to characterize the full matrix and a combination of techniques is required to get insights in the molecular composition.

Oasmaa et al. [105–106] characterized oils using a solvent fractionation scheme. This method successfully enables the observation of major chemical changes in the oils. The fractions are labeled extractives as the ether solubles and insolubles, dichloromethane solubles and dichloromethane insolubles. All fractions are enriched in certain component classes. For the components present in these individual fractions, the reader can refer the work reported by Oasmaa et al. [105–106].

Suping et al. [107] studied bio-oil and its upgrading and concluded that, it was very difficult to determine how the chemical compounds convert during deoxygenation. However, from the Fourier transform infrared (FTIR) spectra in the range, 3200–3500 cm^{-1} a significant diminishing of the –OH group in the upgraded oil can be seen.

7. Conclusions

From the entire literature reviewed in the present paper, it can be seen that, biomass and waste biomass has great potential for conversion to transportation fuels through fast pyrolysis and subsequent upgrading processes. Bio-oil contains a large amount of high molecular weight oxygenates and a minimal amount of hydrocarbons. Bio-oil from fast pyrolysis tends to possess heating value, 19–22 MJ/kg as well as increased oxygen and moisture contents of 45–60% and 25–60%, respectively. Water can be removed from the bio-oil through various techniques. Literature survey reveals that, high level of water reduction can be achieved through solvent extraction [38].

Various catalysts have been utilized for the valorization of bio-oil, as it is composed of both heavy and oxygenated compounds. Therefore, the appropriate catalysts should be one which is having ability to crack bulky molecules and remove oxygen as a heteroatom. If a zeolite were used as the support of a hydrogenating metal, both cracking and oxygen removal would occur. From the reviewed literature, it appears that ZSM-5 possesses ideal characteristics for a support that promotes cracking. Furthermore, traditional hydrotreating catalysts appear to be the most successful and commonly used catalysts in reduced oxygen content and producing valuable transportation fuel range hydrocarbons. In order to avoid loss of surface area, pore volume and activity loss due to blockage of pores by deposits on the catalyst surface, proper selection and design of suitable catalysts is extremely important in bio-oil upgrading process.

Much research still needs to be completed in this field. The standardized testing methods for bio-oil and its products need to be formed. Further, more catalysts should be explored to find salient features; engine and combustion testings should be done to ensure whether transportation fuels are able to meet

specs or blend with petroleum-derived hydrocarbons. However, as can be seen, great progress has already been made in the area of bio-oil valorization which will contribute in the enhancement of potential use of biomass/waste biomass as an energy source, in future bio-refineries.

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